022

GPO PRICE $ ____________

CFSTI PRICE(S) $ ____________

Hard copy (HC) _

Microfiche (MF) _

ff 653 July 65

THE THERMAL RADIATION CHARACTERISTICS OF SOME HIGH-EMITTANCE COATINGS FOR SPACE APPLICATIONS

By B. W. Lewis, W. R. Wade, W. S. Slemp, and D. J. Progar

NASA Langley Research Center
Langley Station, Hampton, Va.

Presented at the ASM Meeting - Session on Coatings

Chicago, Illinois
October 31-November 3, 1966

[redacted]

The Thermal Radiation Characteristics of Some High-Emittance Coatings for Space Applications

B. W. Lewis, W. R. Wade, W. S. Slemp, and D. J. Progar

The results of two investigations of selected factors which may influence the thermal radiation characteristics of high-emittance coatings are presented. One study was to determine the effects of the thickness of ceramic coatings on their high-temperature emittance, and the other study was to investigate the effects of simulated space environments on the emittance of inorganic coatings at moderate temperatures. Four flame-sprayed ceramic coatings of various thicknesses on high-emittance substrate were found to have varying emittance with thickness if the ceramic was semitransparent. A variety of inorganic coatings were evaluated as to their stability of thermal radiation properties to the major space environments. As a result, two excellent candidate coatings for space application were found and characterized. Information as to the types and amount of change due to environmental exposure for these types of coating is presented.

The authors are associated with the NASA Langley Research Center, Langley Station, Hampton, Va. This paper is scheduled for the ASM Meeting - Session on Coatings, Chicago, Ill.

L-5157

Introduction

High-emittance coatings find applications in several areas of space vehicle design. The primary area is that of temperature control where they may be used to absorb energy when facing the sun or other warm bodies or used to radiate energy when facing toward cold space. Other uses include black walls of optical systems, surfaces of radiation detectors, collectors and radiators for space solar or nuclear power systems, and walls of space simulators.

In general, not enough is known about the effects of coatings parameters and environmental exposures on the thermal radiation characteristics of coatings to assure design of reliable space vehicle systems. We have been investigating effects of various factors on the emittance of materials and coatings for a number of years with emphasis on high-emittance coatings. It is the purpose of this paper to present the results of two of our most recent investigations which demonstrate the type and extent of effects of several factors on the thermal radiation properties of some selected coatings. The two studies are presented as separate sections because the type of effect and probable applications are different. One study was to determine the effect of thickness of ceramic coating and substrate condition on the high-temperature emittance. The other study was to investigate the effects of simulated space environments on the absorptance and emittance of primarily inorganic coatings for moderate-temperature space vehicle applications. The common interest in these two studies was to obtain information on the behavior of coatings under various conditions to aid in the selection of thermal control coatings for aerospace uses.

Symbols and Definitions

a	absorptance, the ratio of energy absorbed by a body to that absorbed by an equivalent black body at the same temperature
e	emittance, the ratio of energy emitted by a body to that emitted by an equivalent black body at the same temperature
r	reflectance, the fraction of incident energy which is reflected by a body
t	transmittance, the fraction of incident energy which is transmitted through a body
$e_{\lambda N}$	the spectral, normal emittance, the value for one wavelength normal to the surface
e_{TN}	the total, normal emittance, the value obtained by integration of spectral data over the total wavelength of interest
a/e	the ratio of solar absorptance (a_s) to thermal emittance (e_t) of body where a is the value obtained by integration over the 0.25 to 2.6μ wavelength range and e is the value obtained by integration over the 3 to 25μ wavelength range (corrected for energy above 25μ)

Pertinent relationships:

Translucent bodies at constant temperature

$$a + r + t = 1$$

Opaque bodies at thermal equilibrium or for monochromatic radiation

$$a = e = 1 - r$$

The Thickness Effects of Ceramic Coatings

Ceramic coatings find aerospace applications for collectors and radiators for space power systems and the cooling of aerodynamically heated surfaces during reentry and atmospheric flight. In these uses operational temperatures as high as 1100° C (≈2000° F) are encountered and generally high absorptance or emittance coatings are required. Some flame-sprayed ceramic coatings have the required high-temperature stability and it was felt that perhaps the emittance could be optimized, or tailored to some extent, by varying some coating-substrate parameters. Thus a study was made of the effects of coating thickness and substrate emittance on the spectral and total normal emittance of the coated system. Four ceramics were chosen, alumina (Al_2O_3), zirconia (ZrO_2), magnesium aluminate ($MgOAl_2O_3$), and chromic oxide (Cr_2O_3). The first three are semitransparent white materials and the fourth is a dark green to black, opaque coating. All have high emittance in the infrared. The substrate chosen was the refractory alloy inconel, which had only moderate emittance when unoxidized but had high emittance when oxidized.

A series of the coatings were prepared, by flame spraying to varying thicknesses of about 4 mils to 40 mils, of each ceramic on initially unoxidized and initially oxidized inconel substrates. Forty mils is about the thickest coating feasible by this method. The spectral normal emittance over the 1- to 15-micron wavelength range was measured at the temperatures 482°, 649°, 816°, and 982° C (900, 1200, 1500, and 1800° F) for each specimen series and comparisons made. Measurements were also made of a thick slab specimen of purified (99.9%) alumina ceramic to obtain a base line value. The measurements were made by a method involving a black-body furnace for heating the specimen and alternately furnishing the black-body reference. The method is described in reference 1.

Figure 1 shows data for the Al_2O_3 (Rokide A) flame-sprayed coatings 5 mil and 42 mil thick on oxidized inconel at 982° C (1800° F). Also included are data for an uncoated oxidized inconel specimen and a 320-mil-thick slab of pure Al_2O_3 for comparison purposes. The figure is a plot of spectral normal emittance with wavelength from 1 to 15 microns.

It can be seen that in the 1 to 7μ wavelength range, the coated system has $e_{\lambda N}$ values between the two extreme reference specimens and as the coating thickness increases, the influence of the substrate decreases. Over the 7 to 15μ wavelength range, the coated specimens tend to follow the $e_{\lambda N}$ values of the pure Al_2O_3 more closely than those of the oxidized inconel. The e_{TN} over the whole wavelength range decreases in the order of increasing thickness of Al_2O_3, i.e., 0, 5, 42, and 320 mils give e_{TN} of 0.88, 0.69, 0.44, and 0.29, respectively. Similar type curves and trends were obtained for intermediate thicknesses and the other three temperatures.

The interactions of coating and substrate appear to be complicated and certainly have no simple quantitative relationship which can explain or predict this type of result.

The other two semitransparent coatings, Rokide Z (zirconia) and MA (magnesium aluminate) show similar characteristics of high-emittance substrates but have different shape curves.

The curves for the opaque Rokide C (chromic oxide) coating are shown in figure 2 for 4-mil and 41-mil coatings on initially unoxidized inconel for 982° C (1800° F) and 482° C (900° F). Again the plot is $e_{\lambda N}$ with λ from 1 to 15μ. It is immediately obvious that the coating is not influenced by substrate since there is no thickness effect, the curves for the 4-mil and 41-mil coatings being essentially identical at both temperatures. These curves also illustrate a characteristic of these materials, that the larger valleys and peaks tend to shift toward lower wavelengths as the temperature increases and also there is a simultaneous broadening of these valleys and peaks. The temperature effect of this on e_{TN} generally is small as is the case here.

Figure 3 summarizes the Rokide A and C data on inconel at 982° C (1800° F). It is a plot of e_{TN} with thickness in mils and shows the single point for oxidized inconel, the data for Rokide C on unoxidized inconel, and Rokide A on oxidized and unoxidized inconel. The e_{TN} for the Rokide A coatings decreased almost linearly from 4-mil to 14-mil coatings and then decreased less rapidly as the thickness increased to 42 mils. The Rokide C however shows essentially no change with thickness and the e_{TN} ramains high. This then illustrates the gross difference in the opaque (Rokide C) coating and the semitransparent (Rokide A) types when flame sprayed on inconel. The difference between Rokide A coatings on oxidized and unoxidized inconel was quite small and probably not significant since it is considered that the process of flame spraying and testing hot in air oxidized the substrate surface to give a high e substrate in both cases.

The conclusions from this study of effects of thickness and substrate emittance on high-temperature, high-emittance ceramic coatings were that spectral and total emittances are dependent on the thickness of semitransparent ceramic coating and the total emittance can be varied as much as 50% permitting some degree of tailoring of the emittance within a single coating system. Opaque ceramic coating systems do not possess this flexibility in properties.

Effects of Space Environments on Selected Coatings

Thermal control of space vehicles is necessary to maintain critical systems and/or crew within workable temperature limits which may cover a small temperature band included within a general range of 25° ± 100° C.

Passive control systems are used because of their generally good reliability and minimum weight. These systems utilize the radiation properties of surfaces and coatings on the vehicle skin to affect a thermal balance between internally generated energy, incident energy, and energy radiated from the vehicle. Due to the great variety of missions planned, a wide range of thermal radiation characteristics for surfaces and coatings needs to be available for the production of reliable thermal control systems (ref. 2). In general, thermal radiation characteristics for this use can be grouped in four idealized spectral types each with appropriate a/e ratios as shown in figure 4; flat absorber, solar absorber, flat reflector, and solar reflector. The solar wavelength region is from 0.25 to 26 microns and the thermal wavelength range is from 3 to 25 microns. The a/e ratio, the solar absorptance to thermal emittance ratio, is the radiation parameter generally used in thermal control design work. In this paper only the flat absorber and/or solar absorber were considered to be represented among the coatings studied since the coatings were selected to have high emittance and were black in the visible wavelength range.

The selection of a surface or coating for thermal control depends on several important material properties. First it must have the appropriate a/e ratio to produce the mean skin temperature required by the onboard systems and/or crew. Mean skin temperature is directly related to the a/e of skin. Second, and related to the first, it should be of the particular spectral type required to keep the temperature extremes within allowable limits since the magnitude of temperature oscillations increases with increasing e_t for any given a/e ratio (ref. 3). For example, both flat absorber and flat reflector have an a/e of 1 but the flat absorber would have larger temperature fluctuations than the flat reflector for a given orbit. Third, the surface or coating must possess the physical properties that will assure reliable performance for an extended time in space. Thus the coating must be capable of withstanding long-term exposure to high vacuum, intense ultraviolet radiation, particulate radiation, and micrometeoroid impacts (erosion) without significant change of thermal radiation properties. Other factors which need to be considered are the adherence of the coating to substrate when subjected to thermal shock or mechanical stress, and resistance to mild abrasion.

In order to find one or two flat absorber coatings which would be stable to space environment and to gain knowledge of the type and extent of effects of space environment on this type of coating, we studied a group of black coatings which were selected to be predominantly inorganic in composition and of generally high emittance.

The coatings included in this study were anodized 2S aluminum blackened by inorganic dyes of bismuth sulfide (Bi_2S_3), cobalt sulfide (CoS), lead sulfide (PbS), nickel disulfide (NiS_2) and two commercial organic dyes Sandoz BK and OA, electrodeposited nickel black on aluminum, three chemical-reaction-type coatings for blackening of stainless-type alloys, and two high-temperature paints. The specimens were prepared with deliberate care to produce coatings of reproducible properties. The resultant specimens had a variety of thicknesses which depended on the optimum coating processes for each particular coating system. These specimens were then exposed to various space environments and mechanical tests and evaluated for changes in a/e ratio.

The spectral radiation data were obtained at room temperature ($\approx 25^{\circ}$ C) by measuring the $a_{\lambda N}$ over 0.25 to 2.6μ wavelength range with a commercial-type integrating sphere spectroreflectometer and $e_{\lambda N}$ over the 1 to 25μ wavelength range by means of a heated hohlraum spectroreflectometer. Both of these are considered standard methods for the wavelength regions stated. The thermal radiation data obtained were used to characterize and compare the coatings by utilizing curves of $e_{\lambda N}$ against wavelength in microns and total integrated values of solar absorptance over the 0.25 to 2.6μ wavelength range and total integrated thermal emittance over the 3 to 25μ wavelength range. Figures 5 and 6 show curves of $e_{\lambda N}$ against λ for several representative coatings studied, along with their a/e ratios. These are for specimens which had not been exposed to simulated space environments and show some of the types of spectral curves which may be encountered. It should be noted that there is a scale change in wavelength between the solar and thermal regions. Figure 5 shows the curves for three anodized aluminum coatings, dyed with NiS_2, CoS, and Sandoz OA and one chemical reaction coating, Du-lite 3-0 on type 304 stainless steel. It can be seen that the curves vary widely in shape. The NiS_2 and CoS dyed anodized aluminum coatings are reasonably flat and can be considered to be flat absorbers, the other two however have relatively large absorption bands which characterize their spectra. The a/e values as shown vary from 0.93 to 1.47. Figure 6 shows the same type curves for four other coatings, three chemical reaction coatings and one paint. Here the sodium dichromate ($Na_2Cr_2O_7$) blackened inconel X and Westinghouse black on inconel have high flat solar absorptances but fall off in the infrared regions. The black nickel plate on aluminum and pyromark paint on inconel show very irregular curves which are more representative of complex compositions. The a/e ratios for these coatings range from 0.80 to 1.40. Of the coatings studied only the anodized aluminum dyed with CoS and NiS_2 had flat absorber characteristics and a/e values close to 1. None of these coatings appear to approximate solar absorber-type characteristics.

Having established the initial thermal radiation properties of the coatings of the study, the next step was to expose them to the simulated space environments and check those properties for changes due to exposure.

The simulated space exposure to vacuum was in the pressure range from 2×10^{-6} to 8×10^{-8} torr and total duration was from 300 to 500 hours. The ultraviolet exposure was carried on simultaneously with the same specimens, during the vacuum exposure which was accomplished in two exposure periods of about equal duration. The ultraviolet radiation source was a B-H6 mercury vapor UV lamp placed in the vacuum chamber at such a distance from the specimen to radiate with an intensity equivalent to 10 solar UV constants and producing exposures of from 3440 to 4930 equivalent solar hours at 1 mean earth-sun distance. The electron radiation was performed in air by exposing each of the UV and vacuum exposed specimens to a spread beam of 1 MeV electrons for total doses of 10^{12}, 10^{13}, 10^{14}, and 10^{15} electrons/cm^2 which would be equivalent to about 1 year below or at the inner edge of the radiation belts.

The micrometeoroid erosion test was performed in air by exposing a separate set of coated specimens to the high-velocity fragments from a shaped charge explosion of a cast iron cylinder. The estimated exposure was equivalent to about 300 years in a near-earth orbit based on examination of the specimens and available micrometeoroid flight data.

A composite look at the results of the environmental exposure tests is given in figure 7 where the bar graph shows the percent change of a/e for each coating with two types of exposures (1) combined UV, vacuum, and electron radiation and (2) micrometeoroid. It can be seen that 2 of the 13 coatings showed essentially no deterioration in radiation characteristics due to these exposures while 6 showed various small amounts of change.

The electron radiation damage was very slight or immeasurable in all cases, thus the changes of the first kind shown in figure 7 were those due to UV and vacuum exposure primarily. Since the UV and vacuum exposure took place in two increments, the solar absorptance was determined between the exposures. For most of the coatings the greatest change in a_s took place during the first of these exposures. It is therefore considered that additional changes would be negligibly small for additional times of exposure to UV and vacuum. Consulting figure 7 again it can be seen that the a/e changes for the UV and vacuum exposures are positive for all of the anodized coatings and this can be correlated with data which showed the a_s to increase with exposure while the e_t remained about the same. This change was accompanied by a change in appearance of the coatings from a glossy to a dull finish which was evidence of an increase in roughness which would explain the increase in a_s. The fact that there was no significant change in the shapes of the $e_{\lambda N}$ with λ curves indicates that no important change in composition had taken place. For the other types of coatings the changes in a/e due to UV and vacuum exposures were both positive and negative and no explanation has been found for those effects.

Again consulting figure 7, micrometeoroid damage is indicated in 7 of the 13 coatings and gave both positive and negative effects. These can be explained by the nature of the craters which were produced in the specimens by the exposure test. Those coatings having negative changes (lower a_s and/or higher e_t) were thin coatings in which the cratering exposed bare metal either in the shallow crater or by chipping off of the coating around the crater. Those giving higher a/e were ones with thicker coatings which did not expose bare metal and tended to produce a rougher hence higher solar absorptance surface while the e_t remained about the same or decreased.

Thus far we have been discussing the results from the a/e change viewpoint, but we should bear in mind that the exposures plotted in figure 7 were of varying equivalent space duration. Thus for practical purposes the changes which were less than 4% were of almost negligible size and those coatings would be stable enough for an average length mission. In the case of the micrometeoroid exposures, if one extrapolates back to durations of the order of 5 to 10 years, all the coatings would be satisfactory.

The final consideration of the study was a determination of the relative coating integrity. This was done by a series of tests and measurements which included an abrasive grit blast test to give relative abrasion resistance, a thermal shock test consisting of 10 cycles of heating and quenching, and a bend test and microscopic examination before and after thermal cycling to indicate adherency and flexibility of the coating. All coatings were judged to perform satisfactorily in these tests.

In conclusion, these studies of coatings for moderate temperature uses have disclosed two high-emittance black coatings with flat absorber characteristics which appear to be quite stable to major space environments and which have satisfactory coating integrity. All factors considered, the NiS_2 and the CoS dyed anodized coatings appear to be excellent candidates for space use where a/e values of about 1 and flat absorber characteristics are required.

The study has yielded information on the type and extent of effects of simulated space environments on this type of thermal control coating. Changes in a/e can be either positive or negative depending on the type of effect but changes observed in this study were mostly positive and indications are that physical rather than chemical changes are the cause of the change. In some cases, combined exposures would produce effects which would tend to cancel each other. For the predominantly inorganic type of black coating studied, the a/e stability to space environments and physical properties are generally rated satisfactory when considered for use on most planned space missions.

Concluding Remarks

This paper has presented the results of two investigations primarily performed to add to the knowledge of factors which influence the thermal radiation properties of coatings which may have aerospace applications. The emittance effects of thickness of ceramic flame-sprayed coatings on a high-emittance substrate were shown to depend on the transparency of the coating. Opaque coatings show no thickness effect. The type and extent of effects of simulated space environments on high-emittance black thermal control coating candidates has indicated the effects to be mostly physical rather than chemical and for most of the coatings studied, negligibly small when considered for most planned space missions. Two stable flat absorber coatings with a/e of about 1 have been found. These studies have furnished information which should be of significant help to space vehicle and space ground simulator designers.

REFERENCES

1. W. S. Slemp and W. R. Wade, "A Method for Measuring the Spectral Normal Emittance in Air of a Variety of Materials Having Stable Emittance Characteristics" in NASA SP-31, Measurement of Thermal Radiation Properties of Solids, 1963, pp. 433-439.

2. J. P. Plunkett, NASA Contributions to the Technology of Inorganic Coatings, NASA SP-5014, 1964, pp. 19-41.

3. F. J. Clauss, Editor, Surface Effects on Spacecraft Meterials, John Wiley and Sons, New York, 1960, pp. 3-34.

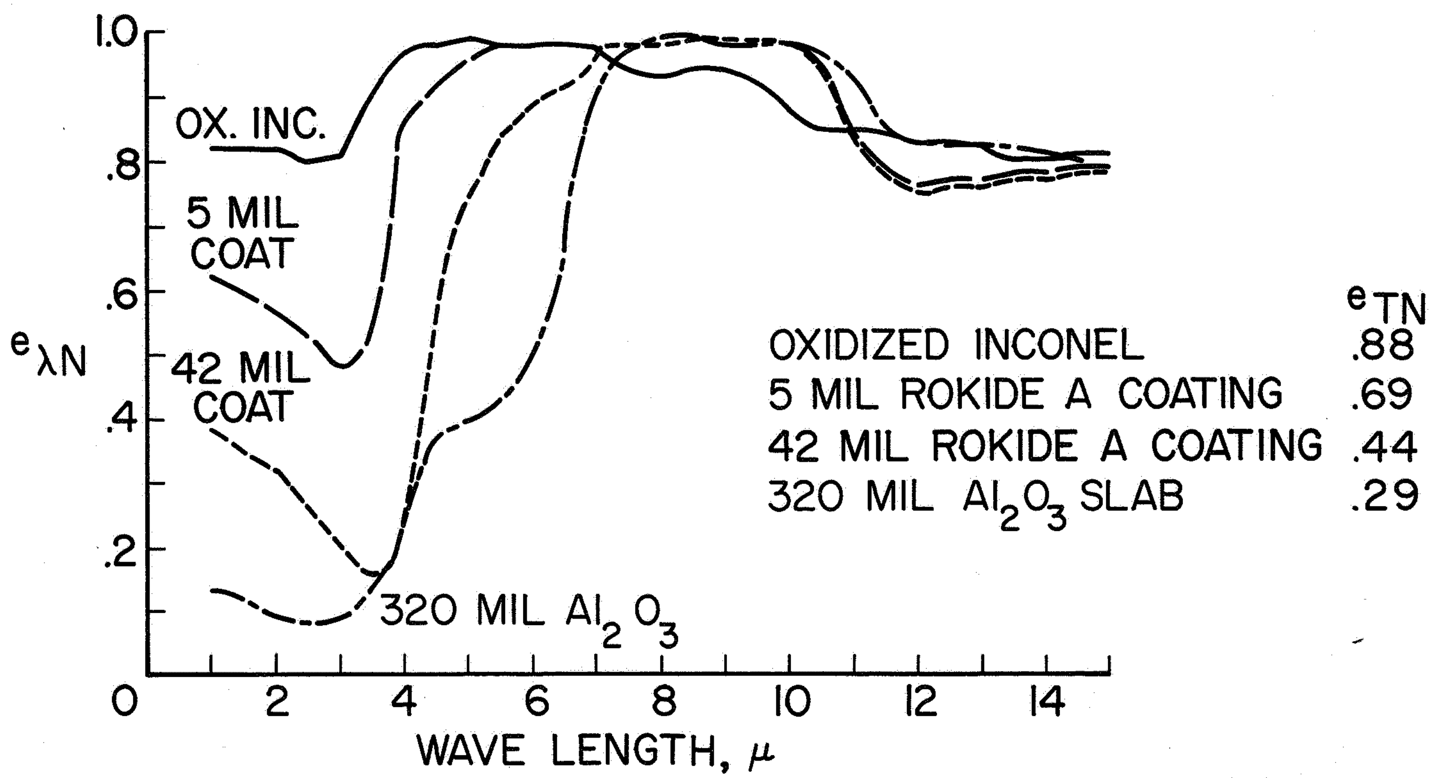

Figure 1.- Rokide A (Al_2O_3) coatings on oxidized inconel at 982° C compared with substrate and thick Al_2O_3 slab.

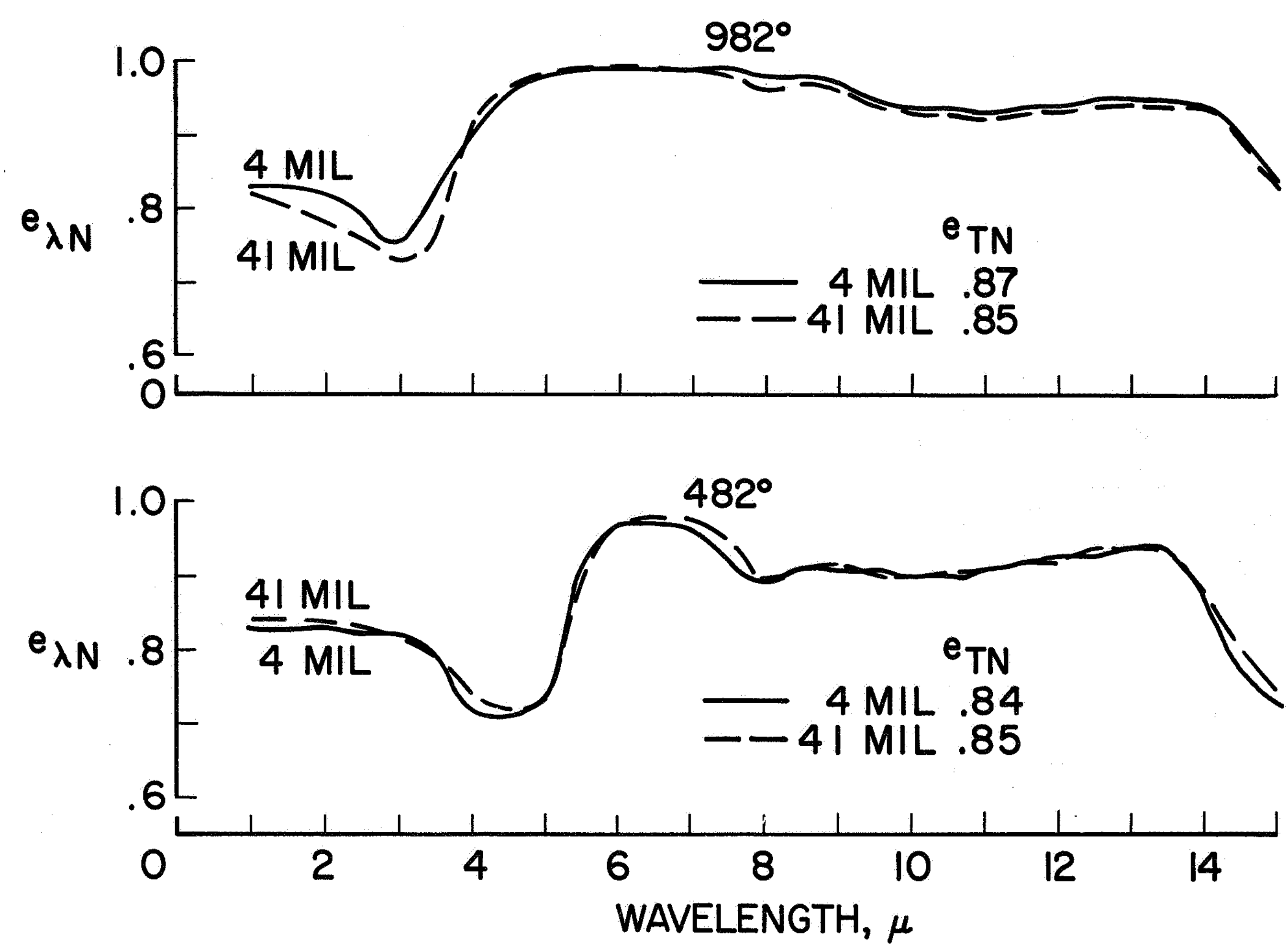

Figure 2.- Rokide C (Cr_2O_3) on inconel at two temperatures and for two thicknesses.

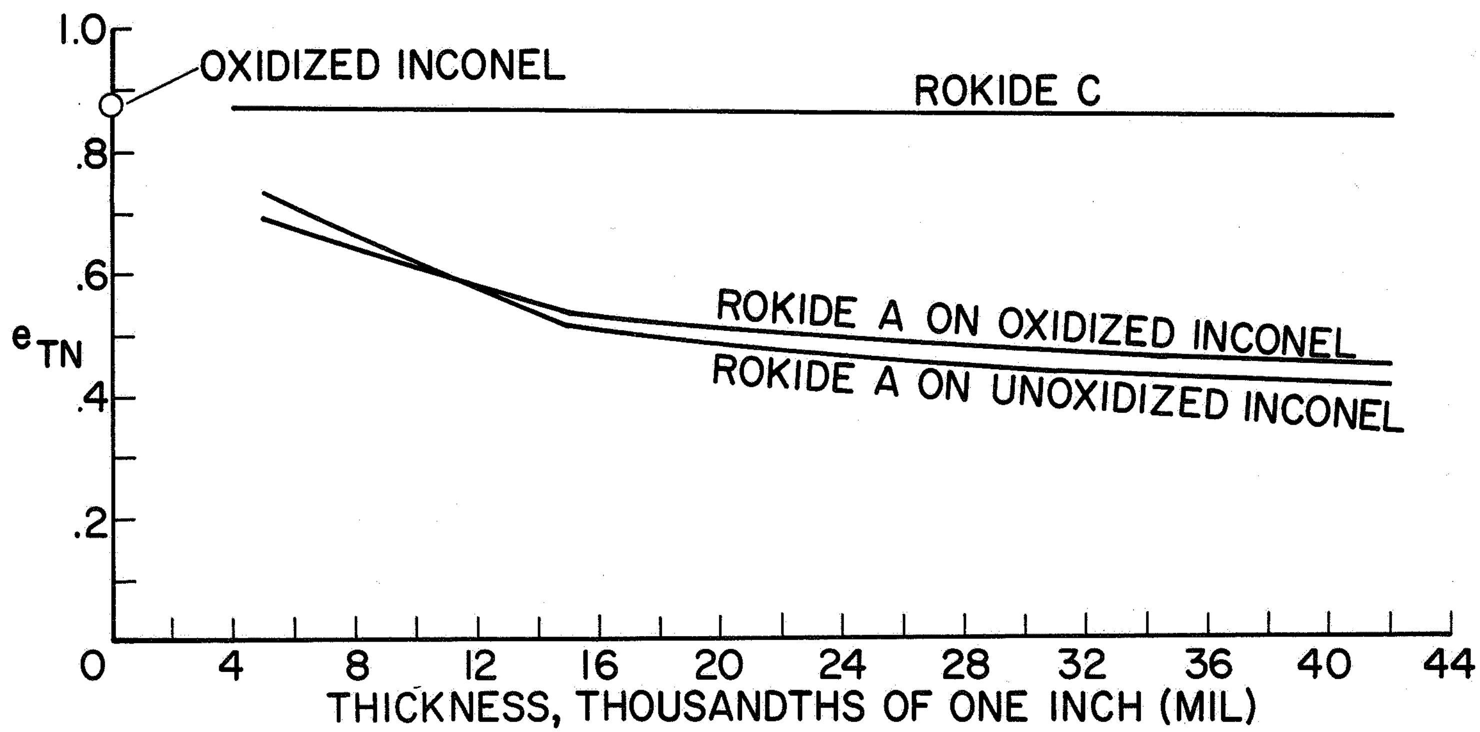

Figure 3.- Changes in e_{TN} with thickness of Rokide coatings, 982° C.

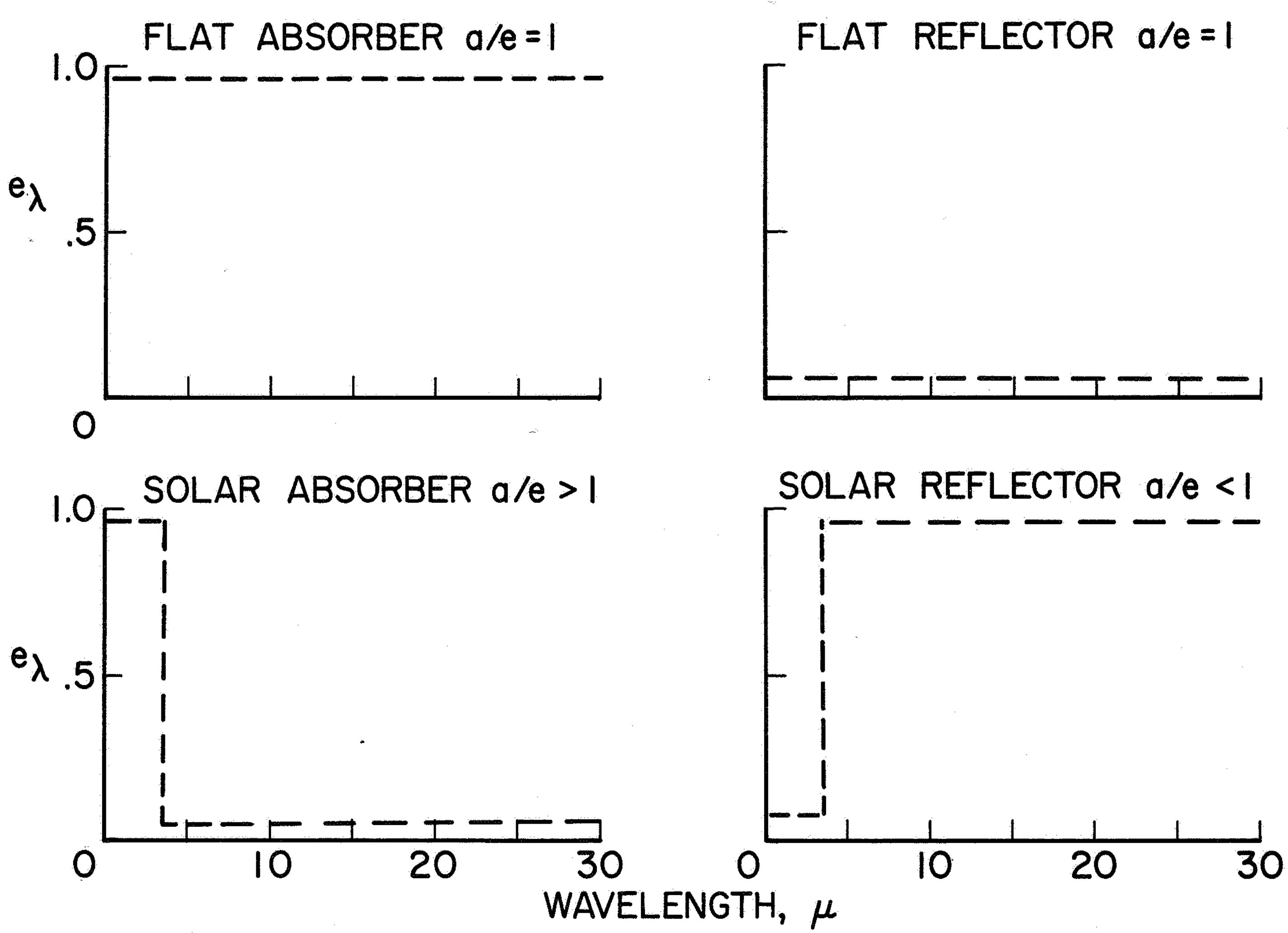

Figure 4.- Four idealized types of thermal control surfaces.

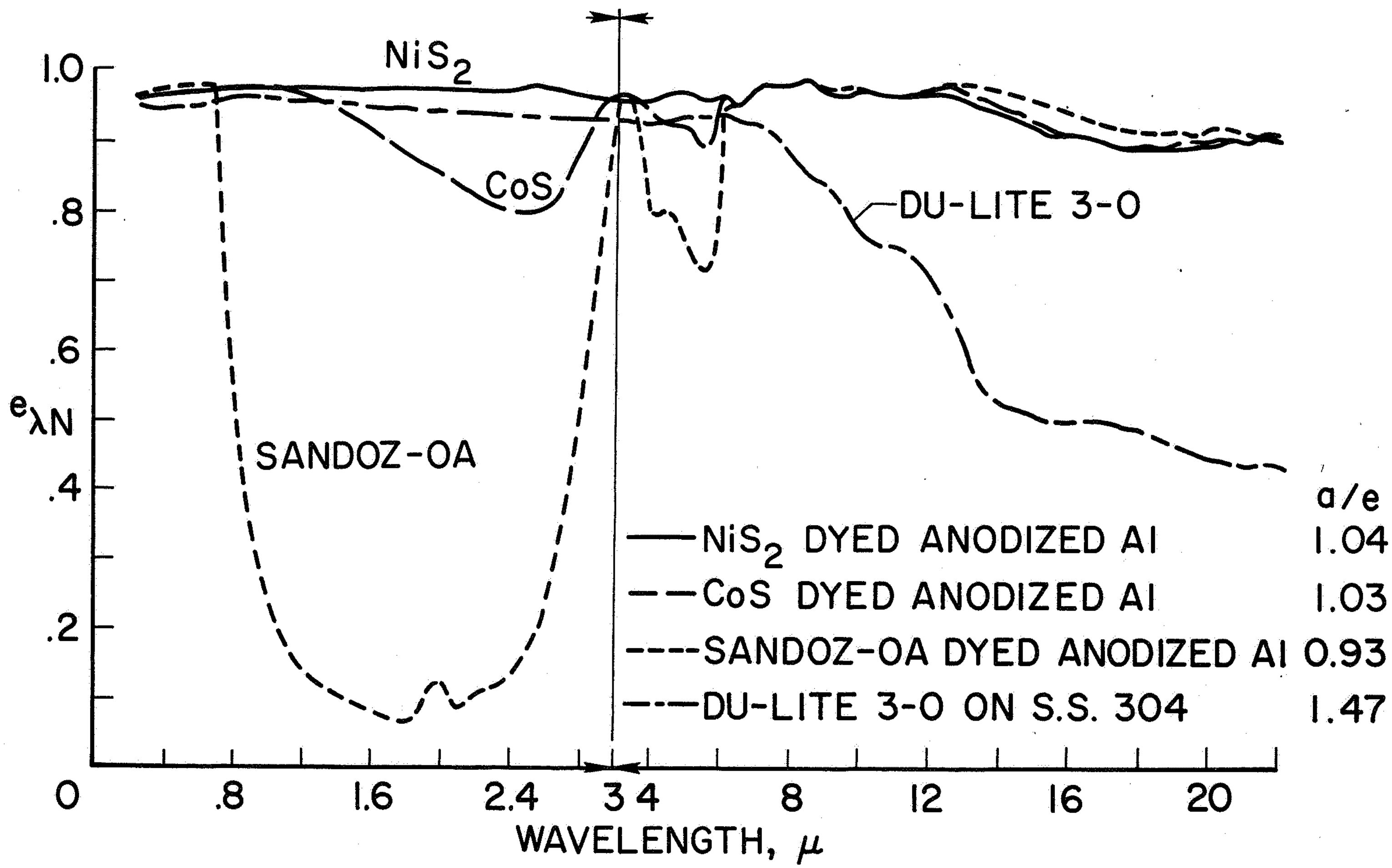

Figure 5.- Spectral emittance of selected coatings at room temperature.

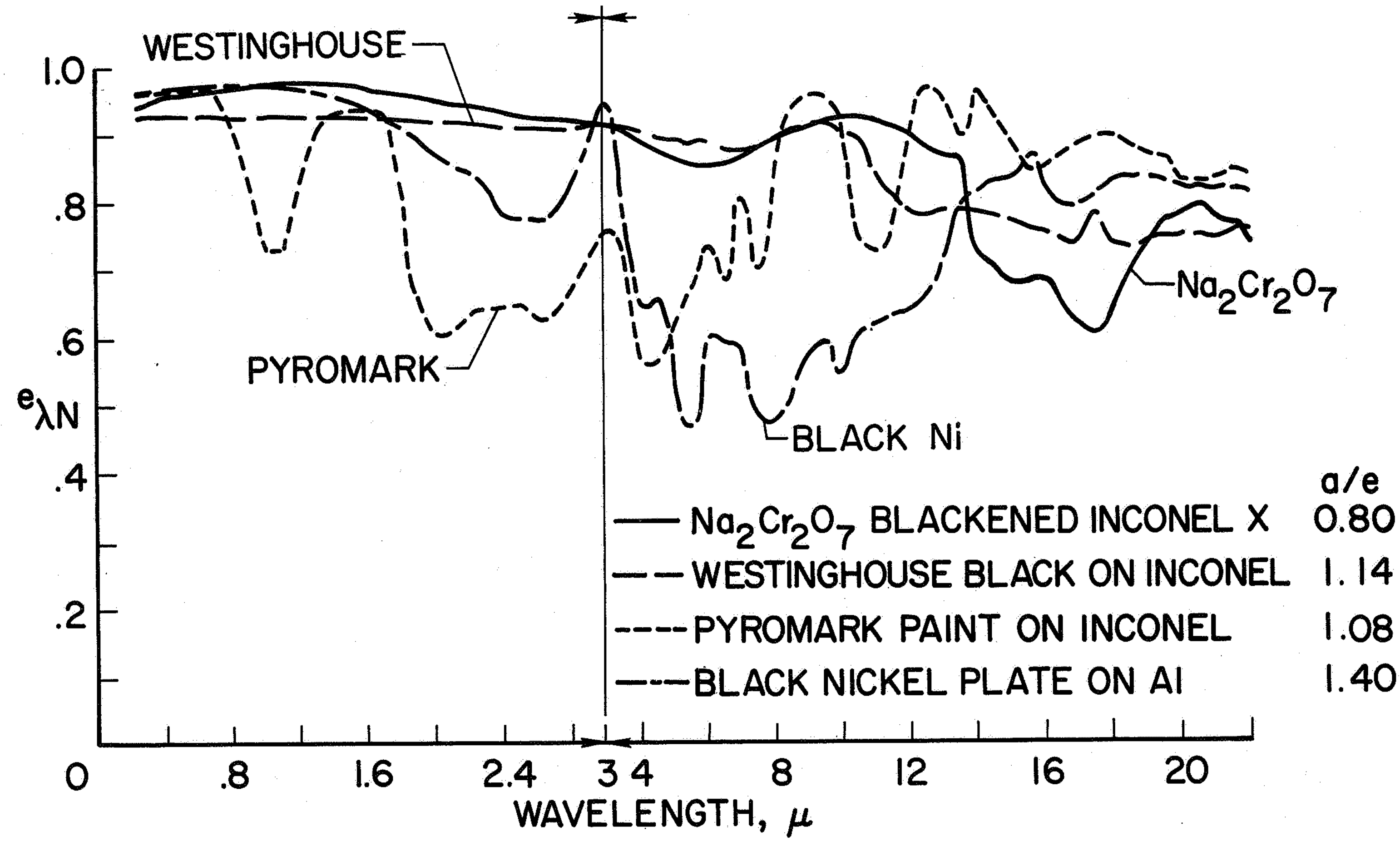

Figure 6.- Spectral emittance of selected coatings at room temperature.

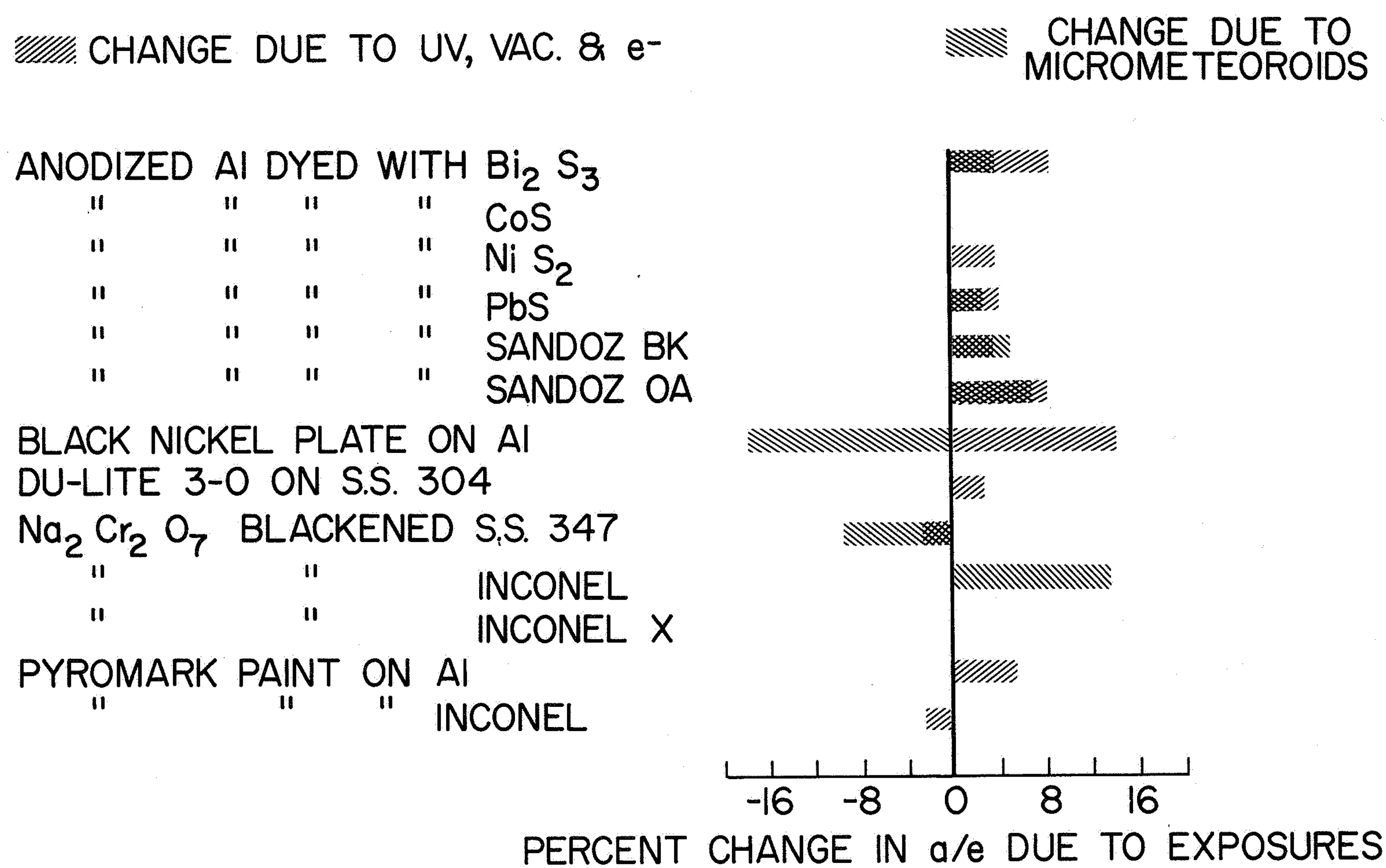

Figure 7.- Changes in a/e ratio due to environmental exposures.

NASA-Langley, 1966